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Physics. — “*The hydrogen isotherms of 20° C. and of 15°.5 C. between 1 and 2200 atms.*” By Dr. K. W. WALSTRA. VAN DER WAALS’ fund researches N°. 8. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of May 30, 1914).

$$T = 20^\circ.$$

§ 1. *Agreement of the observations below 1000 atms. with SCHALKWIJK’S isotherms.*

For each of the series of observations given in the preceding Communication we have determined an empiric equation of the form:

$$PV = a + bD + cD^2 + dD^4.$$

As only series of observations below 1000 atms. can be represented by this equation with 4 virial coefficients, only these series come into consideration for the present. The obtained observation material above 1000 atms. will have to be considerably extended to enable us to calculate the following virial coefficients with the same certainty.

If of the above equation we wish to determine a , b , c , and d , we get a number of equations equal to the number of observations, and consequently then with 4 unknown quantities. To solve these equations according to the method of least squares is not feasible, as then the normal equations become practically identical, which may already be seen beforehand. We have been able to apply Prof. E. v. D. SANDE BAKHUIJZEN’S method successfully, which was also

$T = 20^\circ.$ $\frac{5}{6}$ November 1912.

P	$PV(O)$	$PV(C)$	$(O)-(C)$
959.97	1365.48	1365.48	0.00
744.10	1246.42	1246.43	-0.01
567.53	1146.91	1146.81	+0.10
478.09	1096.26	1096.42	-0.16
377.13	1039.49	1039.49	0.00
296.22	994.18	993.95	+0.23
236.36	960.26	960.42	-0.16
188.42	933.57	933.56	+0.01

$$PV = 829.71 + 445.08 D + 353.40 D^2 + 197.28 D^4.$$

$T = 20^\circ.$ 21 November 1912.

P	$PV(O)$	$PV(C)$	$(O)-(C)$
579.72	1068.76	1068.76	0.00
378.48	963.11	963.11	0.00
283.02	913.49	913.49	0.00
132.69	836.52	936.49	+0.03
129.26	834.66	834.66	0.00
124.90	832.58	832.55	+0.03

$$PV = 770.50 + 371.45 D + 272.26 D^2 + 192.62 D^4.$$

$T = 20^\circ$ 11/12 December 1912.

P	$PV(O)$	$PV(C)$	$(O)-(C)$
787.15	1281.24	1281.25	-0.01
401.68	1061.99	1062.00	-0.01
356.38	1036.25	1036.21	0.04
320.29	1015.72	1015.76	-0.04
295.67	1001.91	1001.81	+0.10
276.70	991.07	991.12	-0.05
245.36	973.55	973.51	+0.04
234.38	967.40	967.35	+0.05
224.36	961.70	961.75	-0.05
214.20	956.05	956.11	-0.06

$$PV = 842.61 + 409.64 D + 423.18 D^2 + 191.36 D^4.$$

$T = 20^\circ$. 10 February 1913.

P	$PV(O)$	$PV(C)$	$(O)-(C)$
962.27	1516.32	1516.32	0.00
638.16	1315.97	1315.97	0.00
469.04	1209.92	1209.92	0.00
216.67	1051.80	1051.80	0.00

$$PV = 923.03 + 508.75 D + 552.10 D^2 + 296.55 D^4.$$

used at Leyden for the calculation of AMAGAT's values at the time. (See Comm. 71). In how far we have succeeded in determining the empiric equations may appear from the following tables. We have placed there side by side P , $PV(O)$ — observed pressure and pressure \times volume —, and $PV(C)$ — calculated with the known volume from the empiric equation, $(O) - (C)$ the difference between the product PV following from the observation and that following from the formula.

$T = 20^\circ$. 11/12 February 1913.

P	$PV(O)$	$PV(C)$	$(O)-(C)$
932.37	1469.32	1469.32	0.00
620.57	1279.75	1279.75	0.00
457.19	1179.37	1179.37	0.00
211.93	1029.03	1029.03	0.00

$$PV = 904.53 + 499.85 D + 494.67 D^2 + 298.61 D^4.$$

$T = 20^\circ$. 22/24 April 1913.

P	$PV(O)$	$PV(C)$	$(O)-(C)$
947.76	1209.81	1209.81	0.00
698.53	1086.84	1086.84	0.00
389.22	930.78	930.78	0.00
339.64	905.45	905.45	0.00

$$PV = 732.67 + 358.69 D + 257.51 D^2 + 101.20 D^4.$$

$T = 20^{\circ}$. 4 June 1913.

P	$PV(O)$	$PV(C)$	$(O)-(C)$
740.81	888.01	888.01	+ 0.00
507.30	794.23	794.22	+ 0.01
358.07	734.12	734.12	+ 0.00
147.42	650.71	650.68	+ 0.03
136.13	646.28	646.30	- 0.02

$$PV = 596.07 + 207.24 D + 147.31 D^2 + 34.13 D^3.$$

To find out whether these series of observations are in harmony with each other, they can be brought in correspondence directly. We did so before, and found only a slight deviation between them. Besides it is also possible to try and make all the series of observations agree with SCHALKWIJK's isotherm, and then compare them also inter se. But then there must first be a reason to suppose that it was possible to make these observations agree with SCHALKWIJK's, and this had soon appeared. When in December 1912 only three series of observations had been found, we calculated from that which contained the greatest number of observations (Dec. $^{11}/_{12}$ 1912) an empiric equation from four of the observations, viz. at 787.15, 401.68, 320.29, 276.70 atms.

The other observations of this series appeared to be in good agreement with the found equation:

$$PV = 841.70 + 415.09 D + 414.10 D^2 + 198.16 D^3.$$

Also the two series of observations of Nov. 1912 appeared to be in harmony with this. Then a comparison with SCHALKWIJK's observations was attempted by reduction of the above equation to one with the same virial coefficient: a as SCHALKWIJK, viz. $a = 1.07258$. This reduced equation then becomes:

$$PV = 1.07258 + 0.0,6740 D + 0.0,8569 D^2 + 0.0,6659 D^3,$$

SCHALKWIJK giving:

$$PV = 1.07258 + 0.0,6671 D + 0.0,993 D^2.$$

This equation holds from 8 to 60 atms., ours from 200 to 800 atms., but we are now going to try to extrapolate with respect to the region of the lower pressures in order to compare these extrapolations with SCHALKWIJK's.

The differences are most apparent when the product PV is deter-

mined from the two equations for different values for D , and the products are joined in the following tables. $PV(S)$ is then calculated from SCHALKWIJK's equation with 3 virial coefficients; $PV(P)$ from our provisional equation.

D	$PV(S)$	$PV(P)$	$(P)(S)$	D	$PV(S)$	$PV(P)$	$(P)(S)$
1	1.0733	1.0733	0.0000	100	1.1492	1.1486	-0.0006
10	1.0794	1.0794	0.0000	200	1.2457	1.2427	-0.0030
20	1.0863	1.0864	+0.0001	300	1.3621	1.3573	-0.0048
30	1.0935	1.0936	+0.0001	400	1.4983	1.4963	-0.0020
40	1.1009	1.1009	0.0000	500	1.6544	1.6654	+0.0110
50	1.1085	1.1084	-0.0001	600	1.8303	1.8718	+0.0415
60	1.1162	1.1161	-0.0001	700	2.0261	2.1241	+0.0980
70	1.1242	1.1240	-0.0002	800	2.2418	2.4330	+0.1912
80	1.1324	1.1320	-0.0004	900	2.4773	2.8102	+0.3329
90	1.1406	1.1402	-0.0004				

The deviations found in this way from what follows from SCHALKWIJK's equation with the extrapolations from our provisional equation appeared to be surprisingly small. Only at a density 100 or $P = \pm 115$ atmosphere pressure the difference is greater than 1 per 2000, but this is far outside the region of SCHALKWIJK's observations. At $D = 200$ or $P = \pm 250$ atms. the difference becomes 1 per 400. Later on it diminishes again, and takes opposite sign, but $D = 500$ or $P = \pm 800$ atms. lies again outside the region of our series of observations.

In connection with the mutual correspondence of the series of observations, the possibility of an agreement with SCHALKWIJK has appeared from this.

In order to be able to compare the 7 series of observations inter se, and judge at the same time about the agreement with SCHALKWIJK, we have reduced the 7 empiric equations in such a way that they give $PV = 1.3573$ for $D = 300$. This is then in agreement with the above table. Then the equations become:

I	$PV = 1.06625 + 0.0_373496 D + 0.0_675009 D^2 + 0.0_{12}69144 D^3$	5/6 Nov. 1912.
II	$PV = 1.06917 + 0.0_371540 D + 0.0_872697 D^2 + 0.0_{12}99111 D^3$	21 Nov. 1912.
III	$PV = 1.07375 + 0.0_366523 D + 0.0_687561 D^2 + 0.0_{12}64295 D^3$	11/12 Dec. 1912.
IV	$PV = 1.06920 + 0.0_368353 D + 0.0_685981 D^2 + 0.0_{12}62047 D^3$	10 Febr. 1913.
V	$PV = 1.06893 + 0.0_362806 D + 0.0_681640 D^2 + 0.0_{12}68826 D^3$	11/12 Febr. 1913.
VI	$PV = 1.05753 + 0.0_374726 D + 0.0_677437 D^2 + 0.0_{12}63400 D^3$	22/24 April 1913.
VII	$PV = 1.07341 + 0.0_367205 D + 0.0_686024 D^2 + 0.0_{12}64632 D^3$	4 June 1913.

At 407.19 atms. (300×1.3573) the series of observations have now been reduced in agreement with each other.

From these equations we calculate first the product PV for the densities 100, 200, 300, 400, and 500 for so far as the corresponding pressures lie in the region of observation of the series, and hence agreement may be expected. We then find :

D	100	200	300	400	500
I	1.1491	1.2429	1.3573	1.4961	—
II	1.1491	1.2428	1.3573	1.4963	1.6654
III	—	1.2426	1.3573	1.4959	1.6641
IV	—	1.2423	1.3573	1.4963	1.6650
V	—	1.2419	1.3573	1.4967	1.6653
VI	—	—	1.3573	1.4966	1.6644
VII	—	1.2430	1.3573	—	—
Mean	1.1491	1.2427	1.3573	1.4963	1.6648

Besides with the mutual agreement, we are struck here with the agreement of the mean values PV with those determined provisionally.

We reproduce therefore this part of the table and place the mean values $PV(M)$ by the side.

D	$PV(S)$	$PV(P)$	$PV(M)$
100	1.1492	1.1486	1.1491
200	1.2457	1.2427	1.2427
300	1.3621	1.3573	1.3573
400	1.4983	1.4963	1.4963
500	1.6544	1.6654	1.6648

It remained to draw up an equation which satisfies the last table of the mean values with $a=1.07258$ in accordance with SCHALKWIJK'S isotherm. This final equation drawn up for convenience with five virial coefficients, becomes:

$$(F). \quad PV = 1.07258 + 0.0_36763D + 0.0_688215D^2 + \\ + 0.0_{12}66954D^3 - 0.0_{18}151D^6.$$

This equation not only represents all our observations as well as possible; but the agreement with SCHALKWIJK's results appears to be even better than for the provisional calculation, which is seen from the following table.

D	$PV(S)$	$PV(F)$	$(F)-(S)$	D	$PV(S)$	$PV(F)$	$(F)-(S)$
1	1.0733	1.0733	0.0000	60	1.1162	1.1163	+0.0001
10	1.0794	1.0794	0.0000	70	1.1242	1.1242	0.0000
20	1.0863	1.0864	+0.0001	80	1.1324	1.1324	0.0000
30	1.0935	1.0936	+0.0001	90	1.1406	1.1406	0.0000
40	1.1009	1.1010	+0.0001	100	1.1492	1.1491	-0.0001
50	1.1085	1.1086	+0.0001				

The final equation may therefore be considered to represent the whole region of the isotherm below 1000 atms. The agreement with SCHALKWIJK is perfect up to $D=100$, which corresponds with a pressure of 115 atms. Reversely it appears therefore that we may extrapolate up to ± 120 atms. from the equation at which SCHALKWIJK arrived from his observations from 8 to 60 atms., viz.

$$PV = 1.07258 + 0.06671D + 0.06993D^2,$$

At $D=200$ or $P=250$ atms. the error which would then be made, becomes already 3 per 1000. For greater densities up to $D=500$ the number of virial coefficients 3 is too small. It must then be 4 at least. It will not do simply to add a 4th coefficient to SCHALKWIJK's equation, which appears from the deviations, which (see table) are now positive, now negative.

§ 2. Comparison of the observations at 15°.5 with AMAGAT's.

We have one series of observations with 4 data below 1000 atms. and three above it at our disposal. (See p. 215).

An equation has been calculated from the 4 data below 1000 as a control of the observations at ± 100 atms. (See preceding communication). To compare our data with those of AMAGAT at 15°.4 we have calculated an empiric equation with 6 virial coefficients from 6 observations. In the seventh observation at 383 atms. we have then a control,

<i>P</i>	<i>PV</i> (O)	<i>PV</i> (C)	(O)-(C)
2255.8	1796.07	1796.07	0.00
1777.2	1582.42	1582.42	0.00
1383.9	1407.15	1407.15	0.00
932.37	1190.26	1190.26	0.00
684.79	1065.47	1065.47	0.00
383.29	916.64	916.66	-0.02
334.27	891.16	891.16	0.00

$$PV = 637.965 + 892.46D - 735.72D^2 + 1215.49D^3 - 787.959D^4 + 204.470D^5.$$

With the value of *PV* at 700 atms. this equation is then reduced to
 $PV = 0.92967 + 0.0_218953D - 0.0_522767D^2 + 0.0_{11}79888D^3 - 0.0_{16}10996D^4 + 0.0_{23}60639D^5.$

The easiest way for the calculation is now to compare the pressures for the same volumes as AMAGAT. We then find:

V	P(Am.)	P(C)	(C)-(Am)
0.002234	700	700	0
0.002046	800	800.5	0.5
0.001895	900	904.7	4.7
0.001778	1000	1005.3	5.3
0.001685	1100	1101.8	1.8
0.001604	1200	1200.7	0.7
0.001533	1300	1301.6	1.6
0.001472	1400	1401.0	1.0
0.001418	1500	1500.9	0.9
0.001370	1600	1601.1	1.1
0.001326	1700	1704.2	4.2
0.001288	1800	1804.2	4.2
0.0012545	1900	1902.6	2.6
0.0012225	2000	2008.0	8.0
0.001194	2100	2113.6	13.6
0.0011685	2200	2220.2	20.2

These deviations and especially the progressive ones above 2000 atms. cannot be explained from the temperature difference of $0^{\circ}.1$, among others on account of their irregularity. This would give a pressure difference of no more than 0.6 atm. at 2000 atms. For the rest the deviations are too large and too systematical to be considered as accidental errors of observation. The most obvious explanation, a systematic error in the absolute pressure measurement made by AMAGAT or by us, cannot be accepted either, as it would yield a deviation proportional for large and for small pressures. Probably the same causes come into play, which also prevented agreement between AMAGAT and SCHALKWIJK's observations.

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Hydrostatics. — “*The different ways of floating of an homogeneous cube.*” By Prof. D. J. KORTEWEG.

(Communicated in the meeting of May 30, 1914).

This problem, whose treatment, however simple it may seem, offers considerable difficulties, was lately brought to a complete solution by Dr. P. BRANDSEN.

If we limit ourselves to the cases in which the specific weight of the cube amounts to less than half of that of the liquid (which is allowed, because the other cases may be derived from it by interchanging the floating and immersed parts) stable floating appears to be possible in four different positions.

In the *first position* four of the edges are vertical. It may be acquired for specific weights, expressed in that of the liquid, smaller than $\frac{1}{2} - \frac{1}{6}\sqrt{3} = 0,211\dots$. For those smaller than $\frac{1}{6} = 0,166\dots$ it is the *only one* possible.

In the *second position* two of the faces are vertical, but the edges belonging to them are sloping. The surface section is consequently a rectangle. This manner of floating is possible between the specific weights 0,211\dots and 0,25.

In the *third position* the space-diagonal of the cube is vertical and the surface section a hexagon. It is possible between the limits $\frac{1}{6}$ and $\frac{5}{6}$ of the specific weight. For the limits themselves the cube is lifted or immersed just so far that the surface section, perpendicular to the space-diagonal, has passed into a triangle. Those limiting positions themselves are already unstable; consequently the stability